

*Citation for published version:*

Francisco, JS, Steinfeld, JI & Williams, I 1986, Thermochemistry, structure and reactivity of the trifluoromethoxy radical. in *NBS Special Publication: Proceedings of the 17th International Symposium on Free Radicals, Granby, CO*. vol. 716, National Bureau of Standards, Washington, pp. 250-255.

*Publication date:*

1986

*Document Version*

Early version, also known as pre-print

[Link to publication](#)

**University of Bath**

## **Alternative formats**

If you require this document in an alternative format, please contact:  
[openaccess@bath.ac.uk](mailto:openaccess@bath.ac.uk)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

**Take down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Thermochemistry, Structure and Reactivity of the  
Trifluoromethoxy Radical

J. S. Francisco and J. I. Steinfeld

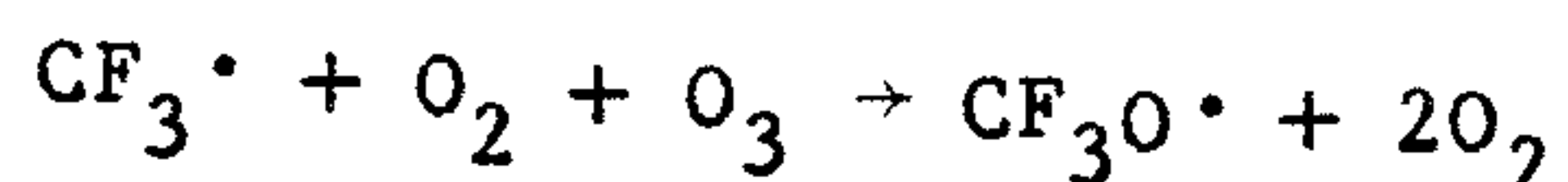
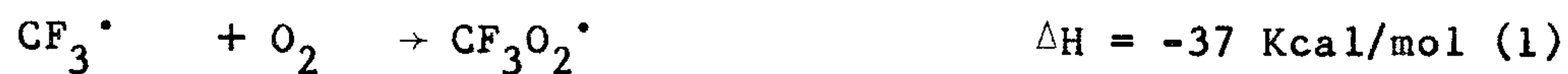
Massachusetts Institute of Technology, Cambridge, Mass. 02139,  
U.S.A

I. H. Williams

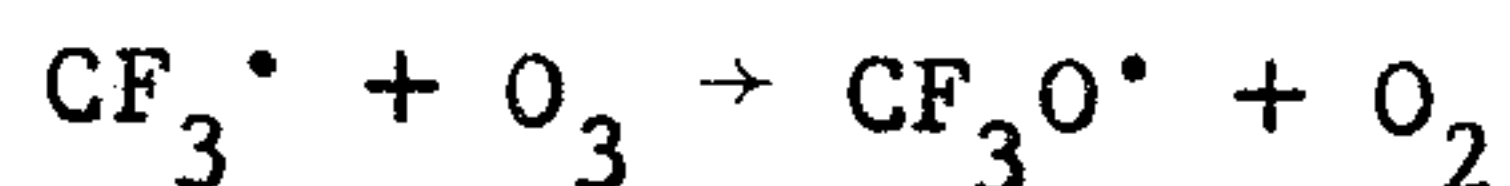
University of Cambridge, U.K.

The importance of halomethanes in the chemistry of the atmosphere relates to their possible threat to the stratospheric ozone layer via photodissociation to  $X\cdot$  and  $CX_3\cdot$  (where  $X = F$  and  $Cl$ ) radicals, but relatively little is known regarding the fate of the latter fragment. In order to investigate the role of  $CX_3$  radicals in the chemistry of the atmosphere, thermochemical estimates [1] have been made for reactive intermediates which may be involved in the oxidation of  $CX_3\cdot$ . In this study we consider the fate of the simplest trihalomethyl fragment,  $CF_3\cdot$ . The reactions of  $CF_3\cdot$  with  $O_2$  and  $O_3$  yield species  $CF_3O\cdot$ ,  $CF_3O_2\cdot$  and  $CF_3O_3\cdot$  for which thermochemical estimates are given in Table 1. On the basis of these estimates, the important atmospheric catalytic cycles involving these species in the destruction of ozone are summarized below:

Cycle I



### Cycle II



However, catalytic destruction of ozone would be possible only if O-atom abstraction (5) is faster than the more exothermic F<sup>•</sup> atom abstraction (6).



Furthermore, the intermediate trifluoromethoxy radical is also a source of fluorine atoms (via reaction 7) which are involved in the catalytic ozone destruction:



From these thermochemical considerations, it is apparent that CF<sub>3</sub>O<sup>•</sup> may be important in CF<sub>3</sub>X oxidation.

There have been several experimental attempts to detect CF<sub>3</sub>O<sup>•</sup>. Christe and Pilipovich [2] attempted to isolate CF<sub>3</sub>O<sup>•</sup> by trapping the products of a low-pressure pyrolysis of CF<sub>3</sub>OOCF<sub>3</sub> in argon at 8 K, but found no evidence for the radical in the matrix. Chen and Kochi [3] studied the photolysis of CF<sub>3</sub>OOCF<sub>3</sub> by electron spin resonance spectroscopy, but CF<sub>3</sub>O<sup>•</sup> could not be detected directly. Rossi et al. [4] studied the reaction of CF<sub>3</sub><sup>•</sup> radicals with ozone, but again the CF<sub>3</sub>O<sup>•</sup> radical was not observed. Infrared multiphoton decomposition of CF<sub>3</sub>OOCF<sub>3</sub> yields trifluoromethoxy radicals [5,6], but as yet these have eluded direct experimental observation. Consequently ab initio quantum-chemical methods have been used to predict the structure and

vibrational spectrum of this radical [7].

Ab initio calculations were performed using the Cambridge analytic derivative package (CADPAC) at the 3-21G level of open-shell theory. The optimized geometries for the low lying excited states of  $\text{CF}_3\text{O}^\bullet$  are given in Table 2. The ground electronic state in  $\text{C}_{3v}$  is degenerate ( $^2\text{E}$ ) and undergoes Jahn-Teller distortion. Geometry optimization in  $\text{C}_s$  symmetry yields stationary points for the  $^2\text{A}'$  and  $^2\text{A}''$  states, stabilized by 0.33 and 0.28  $\text{Kcal mol}^{-1}$  respectively, relative to the  $\text{C}_{3v}$  symmetrical structure. Analytical determination of the second derivatives reveals that the  $^2\text{A}'$  structure is at a true minimum, but the  $^2\text{A}''$  structure is at a saddle point on the potential energy hypersurface. Furthermore, the  $^2\text{A}'$  and  $^2\text{A}''$  structures are connected by pseudo-rotational procession about  $\text{C}_3$  axis of the  $^2\text{E}$  structure. The  $^2\text{A}'$  first excited state of  $\text{C}_{3v}$  symmetry is calculated to be 30937  $\text{cm}^{-1}$  above the ground  $^2\text{E}$  state at the RHF/3-21G level.

Vibrational frequencies and relative intensities for the  $^2\text{A}'$  state are presented in Table 3. These results, along with predicted vibrational frequencies for difluorodioxane [8], now allow us to comment upon the previously published work concerning the formation of  $\text{CF}_3\text{O}$  from the low-pressure pyrolysis of bis-(trifluoromethyl) peroxide,  $\text{CF}_3\text{OOCF}_3$  [2]. Two sets of infrared absorption bands were reported in Ref. 2. One set of bands was still present at 42 K in a controlled-diffusion experiment; these were reported at 1897, 899, 824, 389 and 336  $\text{cm}^{-1}$ . Bands at 1592, 1025, 986, 319 and 268  $\text{cm}^{-1}$  had disappeared and there was uncertainty as to whether bands at 1271, 1076 and 659  $\text{cm}^{-1}$  had also disappeared. It was concluded that at least two different species were involved. The possibility that some of the



unassigned infrared absorptions observed by Christe and Pilipovich [2], following low-pressure pyrolysis of  $\text{CF}_3\text{OOCF}_3$ , might be due to trifluoromethoxy radicals may be discounted on the grounds that those frequencies bear no relation to those calculated for  $\text{CF}_3\text{O}$ . Some of the bands which disappeared at 42 K show a resemblance to those predicted for difluorodioxane, and thus suggest that these bands may be due to difluorodioxane, but the evidence is inconclusive. Nevertheless, one species which might account for the absorptions still present at 42 K is trifluoromethyl fluoroformate, which has strong absorptions at  $1901\text{ cm}^{-1}$  [10]: this compound could be formed according to



Chen and Kochi [3] studied the photolysis of  $\text{CF}_3\text{OOCF}_3$  and though unable to detect  $\text{CF}_3\text{O}^\bullet$  directly using ESR, found evidence for the presence of adducts of  $\text{CF}_3\text{O}$  with alkenes, as in the reaction



These results lend support to the proposed reaction (8) and to the suggestion that  $\text{CF}_3\text{O}^\bullet$  is highly reactive.

#### Acknowledgements

We are grateful to the Cambridge University Computing service for much assistance. JSF would like to thank St. Edmund's House at the University of Cambridge for a Research Fellowship and M.I.T. for a postdoctoral fellowship. IHW would like to thank the Royal Society for a Pickering Fellowship and Clare Hall of the University of Cambridge for a Research Fellowship. This work has also been supported by the Air Force Office of Scientific Research Grant 83-0007.

Table 1

Heats of formation (Kcal/mole) for  $\text{CF}_3^\bullet$  and  $\text{CF}_3\text{O}_x^\bullet$  radicals

Species	$\Delta H_{\text{f},298}^\circ$
$\text{CF}_3^\bullet$	$-112.4 \pm 1.0$
$\text{CF}_3\text{O}^\bullet$	$-156.7 \pm 2.3$
$\text{CF}_3\text{O}_2^\bullet$	$-149.9 \pm 2.2$
$\text{CF}_3\text{O}_3^\bullet$	$-136.6 \pm 3.0$

Table 2

RHF/3-21G optimized geometries and energies for states of the trifluoromethoxy radical

Coordinate	$\text{CF}_3\text{O}^\bullet$			
	$^2\text{E}$	$^2\text{A}'$	$^2\text{A}''$	$^2\text{A}_1$
	( $\text{C}_{3\text{v}}$ )	( $\text{C}_\text{s}$ )	( $\text{C}_\text{s}$ )	( $\text{C}_{3\text{v}}$ )
CO (Angstroms)	1.385	1.383	1.383	1.442
CF <sup>-</sup>	1.332	1.332	1.333	1.316
CF	1.332	1.332	1.332	1.316
$\angle (\text{OCF})^-$ (degrees)	109.9	107.1	112.2	108.5
$\angle (\text{OCF})$	109.9	111.3	108.7	108.5
$\angle (\text{FCF})^-$	109.1	109.5	108.6	110.5
$\angle (\text{FCF})$	109.1	108.2	110.0	110.5

Table 3

Calculated vibrational frequencies and relative intensities for the  ${}^2A'$  ground state of  $CF_3O\cdot$

symmetry	mode	description	Frequency ( $cm^{-1}$ )		relative intensity
			unscaled	scaled <sup>a</sup>	
$a'$	1	CF str., asym.	1444	1256	0.97
	2	CO str.	1397	1251	0.77
	3	CF str., sym.	932	855	0.03
	4	CF <sub>2</sub> wag	641	611	0.08
	5	CF <sub>2</sub> scissor	608	578	0.10
	6	OCF <sub>2</sub> def.	436	399	0.10
$a''$	7	CF str.	1470	1272	1.00
	8	CF <sub>2</sub> rock	636	584	0.02
	9	CF <sub>2</sub> twist	412	202	0.00

<sup>a</sup> Valence force constants scaled by factors determined for  $CF_2O$  and  $CF_3O\cdot$  (CO stretch 0.85, CF stretch 0.79, all bends 0.84); see reference [8].

#### References

- [1] J. S. Francisco and I. H. Williams, submitted to J. Phys. Chem.
- [2] K. O. Christe and D. Pilipovich, J. Am. Chem. Soc. 93, 51 (1971).
- [3] K. S. Chen and J. K. Kochi, J. Am. Chem. Soc. 96, 1383 (1974).
- [4] M. J. Rossi, J. R. Barker and D. M. Golden, J. Chem. Phys. 71, 3722 (1979).
- [5] J. S. Francisco, M. A. Findeis, and J. I. Steinfeld, Intern. J. Chem. Kinetics 13, 627 (1981).
- [6] Fumin Zhang, J. S. Francisco and J. I. Steinfeld, J. Phys. Chem. 86, 2402 (1982).
- [7] J. S. Francisco and I. H. Williams, Chem. Phys. Lett. 110, 240 (1984).
- [8] J. S. Francisco and I. H. Williams, Mol. Phys. 52, 743 (1984).
- [9] J. S. Francisco and I. H. Williams, Chem. Phys. 93, 71 (1985).
- [10] P. J. Aymonino, J. Chem. Soc. Chem. Commun. 241 (1965).  
E. L. Varette and P. J. Aymonino, J. Mol. Struct. 1, 39 (1967).